Phosphate sorption capacities of different substrates in view of application in water treatment systems for ponds

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Abstract

Several substrates have been examined on their phosphate sorption capacity. Wollastonite powder exhibited the highest removal capacity. At all phosphate concentrations the removal was above 82%, with a maximum of almost 96%. The uptake rate was high in the first hour of the batch test and increased with increasing concentration. The wollastonite granules did not take up phosphate at concentrations below 2 mg P/l. At higher concentrations the removal fluctuated between 82 and 96%. Slag exhibited a high absorbing capacity (up to 86%) at concentrations starting from 2 mgP/l. Other materials (ceramic cylinders with active micro-organisms, porphyry and scoria) that were studied did not exhibit phosphate uptake. From this study it is concluded that wollastonite powder has the highest phosphate removing capacity, but that slag is better suited for application in a skimmer, placed as a pretreatment in the water treatment loop of the pond, as the material is coarser.

Keywords

Adsorption, phosphate, fish and swimming pond, water treatment

INTRODUCTION

Fish and swimming pond water needs to fulfil certain phosphate limits in order to limit algal blooms. For fish ponds the limit is set to 1 mgP/l in Flanders (the northern part of Belgium). No such limit exists for swimming ponds, but swimming may be prohibited in case algal bloom is detected visually in order to decrease the risk for toxins. The removal of phosphate can be performed by different techniques such as biological uptake and chemical removal including substrate sorption and precipitation. The biological uptake rate is significantly lower than the rate of chemical removal (Lantzke et al, 1998). The incorporation of phosphate into bacteria is applied in waste water treatment systems using enhanced biological phosphorus removal (EBPR) (Metcalf and Eddy, 2003; Oehmen, 2007). Phosphorus can also be removed by plants in for example a wetland system. Effective disposal is only achieved by harvesting the plants as otherwise the phosphate is released back into the water after biodegradation. Research has shown that between species significant differences exist in phosphorus uptake (Read et al., 2008), but that the uptake lies in the order of 5 g/kg (Greenway and Wooley, 1999). The chemical removal of orthophosphate is called with a general term sorption. Sorption can take place either by precipitation or by adsorption (de-Bashan and Bashan, 2004;

Vymazal, 2007). Phosphates which are immobilised by precipitation are, due to the strong binding, only in a limited degree available for the phosphorus cycle. Adsorbed phosphates on the other hand are less bound and can desorb depending on the environmental factors.
The research described in this contribution focuses on this last technology. The aim is to determine the phosphorus removing capacity for a selected number of substrates in order to find a suitable substrate for application in swimming and fish ponds. The idea is to place this substrate in a skimmer (Wydooghe, 2005). This skimmer can be placed in the water treatment loop of the pond. By reducing the phosphate concentration by sorption, the algal bloom in ponds can be controlled. Removal of phosphorus at low concentrations will be necessary because the phosphate concentration of swimming and fish ponds (0-2 mgP/l) is much lower than that of waste water. Before discussing the results, an overview of possible substrates and their sorption parameters is presented.

Sorption parameters

The binding of phosphate is both dependent on substrate properties and ambient factors. The chemical composition, particle size, pH and phosphorus concentration are some of the factors which exert influence. Although most of the studies discussed below are related to treating waste water, the same conclusions remain valid. However, it should be noted that sorption of phosphate in ponds systems will be lower because of the limited available driving force

Substrate properties

The chemical composition of the substrate plays an important role. The Ca- (Del Bubba et al., 2003), Fe- (Boujelben et al., 2007) and Al-content (Sakadevan and Bavor, 1998; Okada et al., 2007) of substrates appears determinative. Generally these metals are present as oxides. Negative charged phosphate ions can bind to these oxides, as a result of which the available phosphate concentration in water decreases. Sorption is as such a finite process: once the binding places are occupied, no more phosphate removal will occur. Also physical properties influence sorption. Phosphate sorption increases for example with decreasing particle size. Seo et al. (2005) showed that for a filter medium with respective particle sizes of 4-10 mm, 2-4 mm and 0.1-2 mm, sorption of 7.7, 11.6 and 22.5 mgP/kg occurred. The pore also plays a role as sorption increases with increasing pore diameter and pore volume. A substrate with an average pore volume of 0.44 cm^3/g will take up 11 mg P/g. If this pore volume increases up to 1 cm^3/g then 17 mg P/g to will be taken up. A possible explanation for this is that larger pores are less rapidly clogged by sorption and that therefore phosphate can be sorbed longer (Khadhraoui et al., 2002).

Ambient factors

The pH is an important ambient factor. Changes in pH bring about changes in the charge distribution and this will influence the binding strength of phosphate. The optimum pH for sorption differs in several studies (Mustafa et al., 2008; Boujelben et al., 2008; Georgantas and Grigoropoulou, 2007). However, substrates containing Fe and Al are best operated with a pH between 7 and 8, while substrates containing Ca show an increasing sorption capacity from pH 5 to 9 (Peng et al., 2007). Not only the pH but also the phosphate concentration influences sorption as phosphate uptake increases with increasing concentration. As such, it is difficult to interpret phosphate sorption experiments obtained with e.g. waste water in view of use in pond systems as the concentration range can differ an order of magnitude. Finally the amount of dissolved oxygen in water plays a role. Especially Fe would be sensitive for changing oxygen concentrations. At oxic conditions, Fe can be present as Fe(OOH), which has a very large sorption capacity for phosphorus. Changing conditions from oxic to anoxic leads to a 50% decrease of phosphate sorption (Gomez et al., 1999).

Possible substrates

Substrates which are suited for phosphate sorption can be subdivided in 3 categories: natural products, industrial by-products and artificially produced substrates (Westholm, 2006). Comparison of results is difficult because these substrates were tested under different conditions, set-ups and phosphate concentrations. In this contribution, only a listing will be given of tested substrates. Natural substrates can be subdivided into minerals and soils. If a mineral contains Al, Ca and/or Fe in substantial amounts, then it can be assumed that the mineral can be used for phosphate sorption. Examples of such minerals are wollastonite, dolomite and clay. Brooks et al. (2000) reported 100% phosphate removal after 72 hours by wollastonite powder, at initial concentrations of 5 and 10 mg P/l. For dolomite, during a field study, up to 51% removal was reported (Obarska-Pempkowiak and Ozimek, 2000). With clay only a 4.3% decrease was measured during a field study of Hill et al. (2000). Different Al, Ca and/or Fe-containing soils such as laterite (Fe and Al), marl (Ca) and spodosol (Fe and Al) were already tested during laboratory studies. Removal percentages of these soils are given in Table 1.

Table 1. Overview of phosphate removal percentages of different soil types

Soil type	Initial concentration (mg P / l)	Removal percentage (%)	Reference
Laterite	5 - 10	80 - 90	Wood en McAtamney (1996)
Marl	0 - 10	100	Szögi et al. (1997)
Spodosol	15	6,7	Johansson (1999)

The last group of natural materials are marine sediments. Maerl, a sediment which is formed for a large part by algal sedimentation, contains a high concentration of Ca and Mg-carbonates. Laboratory studies showed that this material has a very high sorption capacity of up to 98% when using a solution of 7.5 mg P/l (Gray et al., 2000). Also shells and shell sand show sorption because of the presence of Ca and Mg-carbonates. These materials can possibly be employed for phosphate sorption. The sorption during batch experiments of Roseth (2000) at phosphate concentrations between 5 and 1000 mg P/l, amounted to 3 to 4 g/kg substrate.

The second group of substrates exists of industrial by-products. Slags, originating from the production of steel contain Ca- and Al-oxides. In batch experiments with phosphate concentrations between 5 and 25 mg P/l sorption of 1000 mg P/kg substrate was demonstrated (Johansson, 1999). Burned oil shale, originating from the production of oil, contains a high concentration of Al. The maximum sorption capacity according to the Langmuir equation is 650 mgP/kg substrate (Drizo et al., 1999). Fly ash contains Al-oxides and has already proven sorption capacities on lab-scale, but no research has been conducted towards practical application. At a phosphate concentration of 100 mg P/l, a sorption capacity of 8260 mgP/kg was measured (Agyei et al., 2002). The artificially produced substrates consist for the largest part of light weight aggregates, used as construction material. These are produced by heating clay above 1000°C. The sorption capacity fluctuates between 200 and 2000 mgP/kg substrate (Zhu et al., 1997).

MATERIALS AND METHODS

Tested substrates

Natural substrates (fine and coarse scoria (8-16 mm en 16-32 mm), wollastonite granules, wollastonite powder, algal powder and porphyry), industrial by-products (slag granules) and artificially produced products (ceramic cylinders with effective micro-organisms) were tested. These materials were selected based on their expected high phosphate removing capacity.
Wollastonite consists of 51% SiO_2 and 41% CaO. The remaining fraction contains several other oxides, each in small quantities. The algal powder consists of CaO and P_2O_5. Porphyry consists mainly of silicate (Si_xO_y), aluminium oxides and (in smaller quantities) Fe, Ca and Mg. Slag is a by-product that originates from the production of iron and steel and consists of Ca-, Si-, Al- and Mg-oxides. The ceramic cylinders (type S) contain effective micro-organisms imbedded in the material at a temperature of 800 to 900°C.

Phosphate solution and analysis

Phosphate solutions were prepared with the following concentrations: 0.1, 0.5, 1, 2, 5, 10 and 20 mg P/l by dissolving the appropriate amount of K_2HPO_4 (Merck, Germany) in aqua destillata (AD). All phosphate solutions were pH corrected to pH 6.
The analysis of phosphate was according to the standard methods (Standard methods, 1992) by a spectrophotometric method. The expected precision of this method is 5 to 10%.

Sorption tests

In order to investigate the possibility of phosphate sorption of each substrate, batch tests at 20°C were performed (Figure 1). 50 g substrate was mixed with 250 ml phosphate solution.

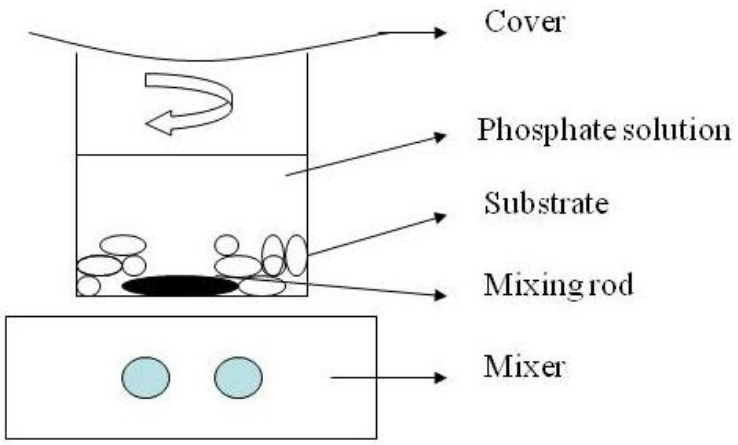

Figure 1. Batch test set-up

After 1, 5 and 23 hours a phosphate measurement (2 duplicates) was carried out. If necessary, stirring was stopped 5 minutes before measuring to allow settling. As such, particle interference of the phosphate measurement was limited.

The Freundlich equation was fitted to the results of the test:

$$\frac{X}{M} = K \times C_e^{\frac{1}{n}}$$

With
X = quantity of sorbed phosphate in mg
M = mass substrate in kg
K = Freundlich coefficient
C_e = end concentration phosphate in g/l
1/n = Freundlich constant
The use of the Freundlich isotherm over the Langmuir isotherm was preferred as the Freundlich isotherm models phosphate adsorption data better (Sakadevan and Bavor, 1998)

RESULTS AND DISCUSSION

Batch tests

Initial testing

The phosphate concentration increased after 5 hours from 1.95 to 17.35 mg P/l when testing the sorption capacity of the algal powder. This increase can be attributed to the chemical composition of the powder. This substrate consists partly of P_2O_5, which is soluble in water at 20°C. As such the algal powder is not considered as suited for the elimination of phosphate and was not further tested. Also the ceramic cylinders did not appear suitable. Even at the highest phosphate concentration of 20 mg P/l no sorption was observed. The test period was extended for these ceramic cylinders, because effective micro organisms could exhibit phosphate removal after an adaptation period. However, after 5 days still no phosphate removal was detected. Adding porphyry to a phosphate solution (1.95 mg P/l (low concentration) and 20.06 mg P/l (high concentration)), did not cause a decrease of the phosphate concentration. As such porphyry is not suited for phosphate sorption. The fine scoria particles (8-16 mm) showed no significant phosphate uptake at concentrations of 5, 10 and 20 mg P/l. The particles were therefore not able to remove phosphate from water. The coarse scoria particles showed no sorption at a concentration of 5 mg P/l. At concentrations of 10 and 20 mg P/l a limited uptake of about 20% was detected. As phosphate sorption was not possible for these substrates, it was decided to no longer study these substrates.

Wollastonite granules, wollastonite powder and slag

Wollastonite granules, wollastanite powder and slag were further tested as these materials showed to have phosphate removing capacities (see below). At low concentrations (0.1 and 0.5 mg P/l), a reduction of the phosphate concentration of respectively 85 and 82% was determined when testing with the wollastonite powder. With the slag a removal percentage of only 15% was obtained at an initial concentration of 0.1 mg P/l. Tests with the wollastonite particles showed a slight increase in phosphate concentration at low concentrations, which can possibly be attributed to the random measurement error (Figure 2). Further the removal rate of the different substrates was different. Wollastonite powder exhibited a higher rate than the other 2 substrates, although the steady state concentration after 23 hours was similar. This can be seen in Figure 2. The results at higher phosphate concentrations are similar for all 3 substrates, although the wollastonite powder exhibited the highest removal capacity. The removal capacities at different initial concentrations are depicted in Figure 3.The physical properties of the substrate play an important role, next to the chemical composition. The influence of the particle size can be illustrated by the results obtained in Figure 3. These results show that for all tested concentrations more phosphate was sorbed by the wollastonite powder, than by the wollastonite particles, as a result of which also the removal percentages are higher.

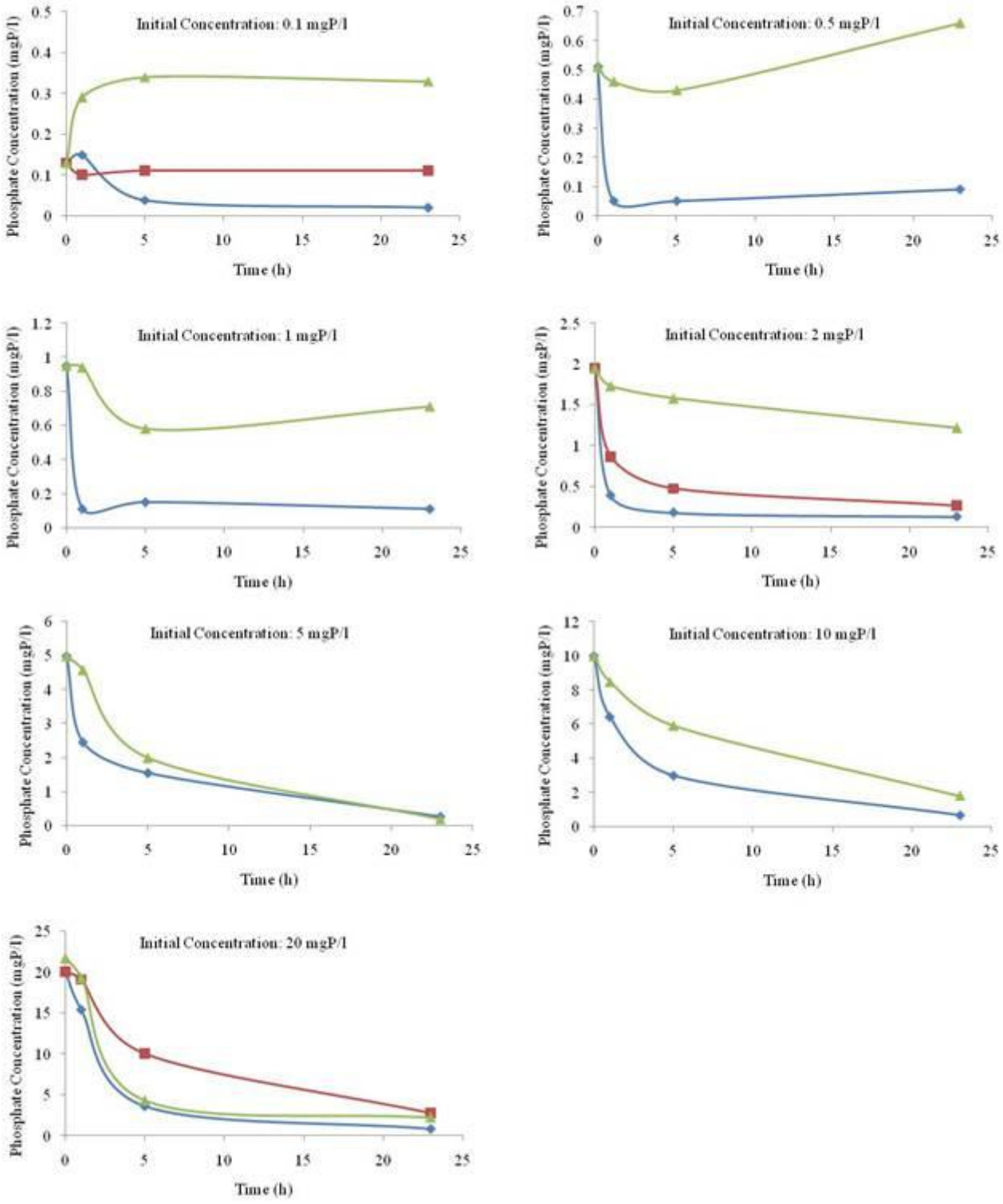

Figure 2: The phosphate concentration as function of time and initial concentration (♦: Wollastonite powder, ■: Slag, ▲: wollastonite granule)

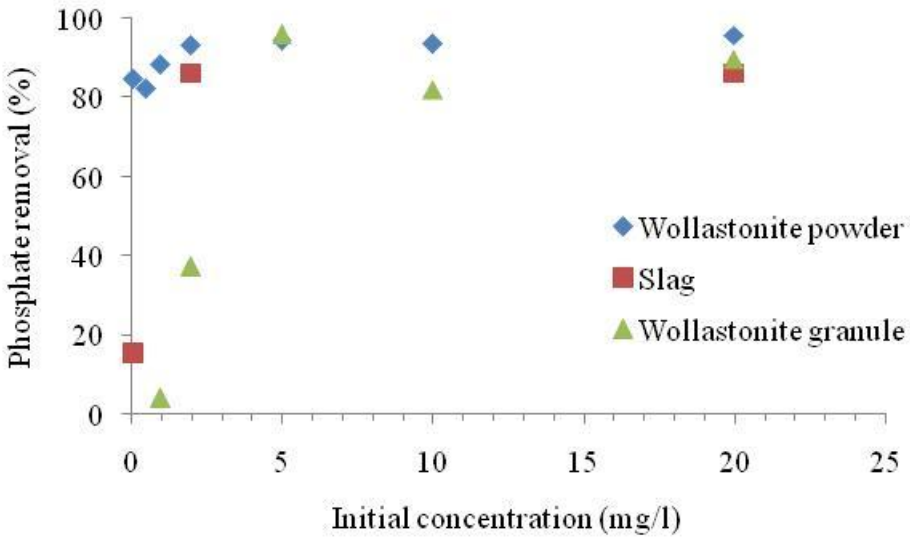

Figure 3. Phosphate removal capacities of wollastonite granules, wollastanite powder and slag as function of the initial concentration

Determination of the sorption capacity

For the determination of the sorption capacity a Freundlich isotherm was used. In Table 2 the Freundlich coefficient and Freundlich constant are given. It can be seen from the table that wollastonite powder has the highest sorption capacity. Further, in Figure 4 the Freundlich isotherms with fitted curves are depicted. A good agreement is obtained although for the slag only 3 measurements were performed.

Table 2: Freundlich-coefficient K and Freundlich constant 1/n of wollastonite granules, wollastanite powder and slag.

Substrate	K (mg P / kg)	1/n
Wollastonite granules	2,92	4,45
Wollastonite powder	123,31	1,63
Slag	28,80	1,08

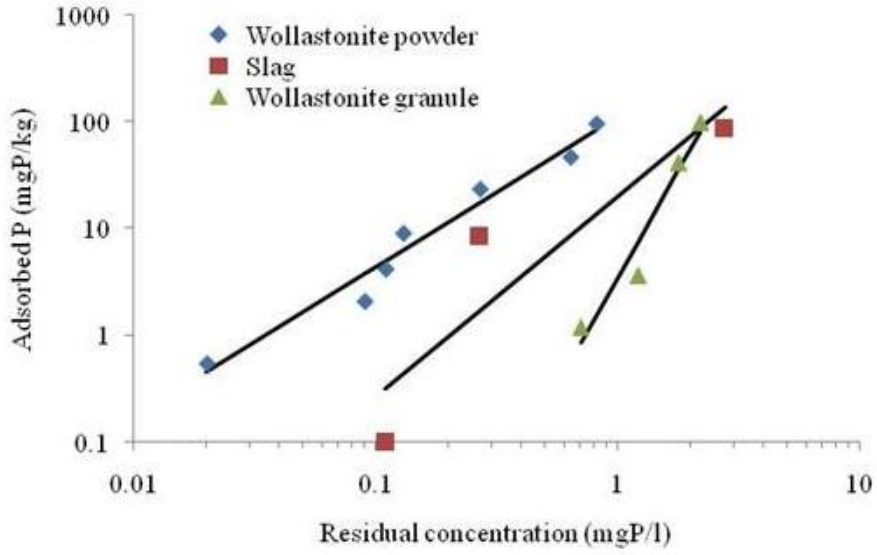

Figure 4: Freundlich isotherms for the adsorption of phosphate on wollastonite granules, wollastanite powder and slag.

Comparison with literature

Brooks et al. (2000) obtained similar results for sorption tests with wollastonite powder as is depicted in Table 3.

Table 3: Comparison of obtained results with literature values (Brooks *et al* (2000)).

	Brooks *et al* (2000)	This study
Removal percentage at an initial concentration 5 mg P / l	100	95
Removal percentage at an initial concentration 10 mg P / l	100	94
Phosphate:substrate ratio	20:1	5:1
Experimental time (h)	72	23

A study of wollastonite particles by Geohring et al. (1999) showed removal percentages up to 68% at phosphate concentrations between 2 and 10 mg P/l. In this study removal percentages up to 96% (at 5 mg P/l) were obtained at the same concentrations levels. A possible explanation for this difference can be the different composition of the wollastonite granules as these natural materials have a varying composition.

Comparison for the slag material is also difficult as here too the composition plays an important role. The source of the slag determines in which quantity each oxide is present. Sakadevan and Bavor (1998) reported removal capacities up to 100% by `blast furnace slag", at initial concentrations lower than 100 mg P/l. In this research the maximum removal percentage was 86%, both at a concentration of 2 and 20 mgP/l.

Concerning the Freundlich isotherm parameters the following conclusion can be drawn. The maximum adsorption capacity expressed by the K-value is significantly lower than that of several other studies such as e.g. Sakadevan and Bavor (1998) because of the lower concentration range applied here. This concentration range was applied because it is typical for swimming and fish ponds. Studies with experiments in this concentration range (0-10 mgP/l) have maximum adsorption capacities (50-390 mgP/kg substrate) within the same range (Prochaska and Zouboulis, 2006; Seo et al., 2005; Boujelben et al., 2008), although the maximum adsorption capacities for slag can be considered to be rather low. Slag will as such be saturated faster. This saturation problem can be circumvented by using an easy to replace skimmer.

CONCLUSIONS

In this research several substrates have been examined on their phosphate sorption capacity. The results of this study are complementary to previous work on phosphate sorption capacity of different materials and focuses specifically on the concentration range of swimming and fish ponds (0-10 mgP/l). It can be concluded that Fe-, Al- and/or Ca containing substrates exhibit the highest sorption capacity. As such these substrates are most suited for use as skimmer for treating swimming and fish pond water.

Wollastonite powder exhibited the highest phosphate removal capacity. At all phosphate concentrations the removal was above 82%, with a maximum of almost 96%. The uptake rate was very high in the first hour of the batch test and increased with increasing concentration. The wollastonite granules did not take up phosphate at concentrations below 2 mg P/l. At higher concentrations the removal fluctuated between 82 and 96%. Slag exhibited a high phosphate absorbing capacity (up to 86%) at concentrations starting from 2 mgP/l, but has a lower maximum adsorption capacity.

From this study it is concluded that, of all the substrates studied, wollastonite powder has the highest phosphate removing capacity, but that slag is better suited for application in a skimmer as the material is more coarse, provided that the slag material can easily be replaced.

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